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# THE REACTION BETWEEN IODINE AND CERTAIN UNSATURATED FATTY ACIDS

BY

HARRY DAVETT GRIGSBY

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

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June 1 1906.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION<sup>#</sup> BY

Harry Davett Grigsby

ENTITLED The Reaction Between Iodine

And Certain Unsaturated Fatty Acids,

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Science.

*Stewart*

HEAD OF DEPARTMENT OF Chemistry.

#- The work of this thesis was done under the immediate direction  
of Dr. James H. Walton, Jr.





THE REACTION BETWEEN IODINE AND CERTAIN UNSATURATED  
FATTY ACIDS.

OUTLINE:-

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## I. INTRODUCTION.

It is well known that the halogens possess the power to break double or triple bonds in unsaturated chain compounds and unite to form addition products. In the case of chlorine and bromine this addition takes place rapidly when the substances come in direct contact or in contact in alcohol and many other solutions. Iodine dissolved in alcohol possesses very little power of breaking the double bond. However in the presence of mercuric chloride iodine adds quite rapidly. Although this reaction is not exactly quantitative it has come to be one of the most important tests applied to fats and oils to determine the amount of unsaturated fatty acids present. The three most important methods of applying this test are those described by Hübl, Wijs, and Hanus. The weight of iodine absorbed is calculated in percent of weight of substance treated and this percentage is called the iodine number. It will be seen later, however, that it is not the iodine addition product which is formed, as the name iodine number would indicate but the iodine chloride addition product.

### a. Historical.

The first method of using iodine for the examination of fatty substances was originated by Baron Hübl in 1884<sup>1</sup>. The solutions he used were prepared as follows:

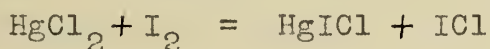
- (1) 25 gms. iodine in 500 c.c. of 95% alcohol free from fusil oil,





- (2) 30 gms. mercuric chloride in 500 c.c. of 95% alcohol free from fusil oil.

These two solutions were united and allowed to stand twelve hours before using. The fat or oil was weighed, dissolved in 10 c.c. of chloroform and 20 c.c. of the above iodine solution added to it. The mixture was allowed to stand two or three hours in the dark and then titrated with N/10 thiosulphate solution. Blanks were run and the difference in titer of the blanks and the test gave the iodine absorbed in terms of the thio-<sup>the</sup>sulphate solution. From this <sup>the</sup> iodine number could be calculated. The active reagent in this reaction is supposed to be iodine monochloride.<sup>2</sup> formed according to the following equation:-



In the Wijs method<sup>3</sup> the solution is prepared as follows: 9 gms. of iodine trichloride are dissolved in one liter of glacial acetic acid (99%) and 5 c.c. of this solution titrated against N/10 thiosulphate solution. From this titration the amount of iodine necessary to convert all the iodine trichloride to iodine monochloride is calculated and added. This solution is used in exactly the same way as the iodine solution in the Hübl process with the exception of the time of reaction which is shortened to from fifteen minutes up to one hour. The advantages of this method over the Hübl method are: the titer of the solution remains much more constant; and the time of reaction is greatly shortened. The results obtained by the two methods agree. The Wijs number seems to be somewhat higher.<sup>4</sup>

In the Hanus method<sup>5</sup> the following solution is used:



20 gms. of iodine monobromide are dissolved in one liter of glacial acetic acid. The fat is weighed, dissolved in 10 c.c. of chloroform and 25 c.c. of the above solution added and allowed to stand 15 minutes before titration. Then potassium iodide solution is added and the solution is titrated against N/10 thio-sulphate solution. The originator of this method claims all of the advantages of the Wijs method together with the advantage that this solution is much more easily prepared. The results agree very well with the Wijs method.<sup>4</sup>

Many other methods and modifications of the above methods have been proposed but none have come into general use.

An interesting method was published by Gill and Adams in 1900.<sup>6</sup> They used a solution similar to Hübl's but with mercuric iodide substituted for mercuric chloride. With this solution they claimed to get the theoretical addition with oleic acid and also an iodine number which agreed very well with Hübl's number for fats. This reaction took from three to five hours for completion. Since there was no other halogen but iodine in the solution there could be no possibility of a compound such as ICl forming. The mercuric iodide therefore played the part of a true catalytic agent.

#### b. Object.

The object of the experimental work performed in this investigation was to study the iodine number using chemically pure substances and standard conditions. The experiments had further for their object the determination of the effects of different





kinds of solvents and catalysers on the reaction and the speed of addition.

c. Reagents Used.

Methyl Alcohol.

The methyl alcohol used was found to be free from acetone by the permanganate test and was distilled from quick lime before using.

Carbon Bisulphide.

The carbon bisulphide was purified by washing twice with a rather strong solution of potassium hydrate, then washing ten or fifteen times with distilled water, drying with calcium chloride and finally distilling.

Oleic Acid.

The oleic acid used was the purest obtainable from Merck and part was purified by myself using the following method.<sup>8</sup> First the Merck oleic acid was treated with ammonium hydrate, quite a large amount in excess of that necessary to change it to the ammonium soap being used. The barium chloride was then added to complete precipitation of the barium oleate. The barium oleate thus precipitated is a white amorphous mass. This barium oleate was recrystallized from ethyl alcohol. This is the most difficult part of the process. When the crude barium oleate is treated with boiling alcohol it fuses to a sticky, yellow mass which is difficultly soluble in the hot alcohol. After boiling ten to twenty minutes the alcohol is drawn off and allowed to cool. The barium oleate separates out in small white crystals.



The yield from one crystallization even when a liter or two of alcohol is used is very small (about 5 gms). This fact makes necessary repeated extractions which are tedious. After the re-crystallized product is obtained it is decomposed by a solution of tartaric acid and the oleic acid obtained washed free from barium salts. The oleic acid is then dried over sulphuric acid in a vacuum desiccator. The oleic acid prepared by this method had a faint yellow color, no odor and melted sharply at  $14^{\circ}$  C. It was evidently a purer product than the Merck sample which had a bright yellow color, a rancid odor and although it melted at  $14^{\circ}$  C. the melting point was not so sharp.

#### Allyl Alcohol.<sup>9</sup>

As the allyl alcohol was not obtainable in this country it was prepared in the following manner: 800 gms. of glycerine and 200 gms. of oxalic acid were put in a liter distilling flask and 1 gm. of ammonium chloride added to decompose any alkali salts present which interfere with the reaction. The mixture was distilled and the portion coming over between  $195^{\circ}$  -  $240^{\circ}$  C. was collected. 120 gms. more of oxalic acid was added and the same fraction collected. The process was repeated using 40 gms. of oxalic acid. The distillates were united and distilled, the fraction boiling below  $105^{\circ}$  C. being collected. The allyl alcohol was then salted out with dry potassium carbonate and separated. 10% of its weight of potassium hydrate was added and then it was allowed to stand two days or until the odor of acrolein had disappeared. It was then separated and distilled. The fraction from  $90^{\circ}$  -  $96^{\circ}$





C. was collected. The last traces of water were removed by allowing it to stand with lime and finally with anhydrous copper sulphate and distilling.

#### Iodine, Mercuric Salts, etc.

The iodine, mercuric salts and other salts used as catalysers were obtained as chemically pure articles from Merck and Kahlbaum.

## II. EXPERIMENTAL.

With the intention of studying the results obtained by Gill and Adams, and determining the speed of addition of iodine and the effects of varying amounts of the catalyser, mercuric iodide, a series of tests were run to duplicate the results which these investigators obtained with oleic acid. At the same time tests were run with cinnamic acid to see if it were possible to get theoretical addition with this simpler compound which could be easily obtained pure.

### a. Experiments with Cinnamic Acid.

The iodine solution used was prepared according to directions by Gill and Adams, i.e. 5 gms. of iodine and 6 gms. of mercuric iodide were dissolved in 200 c.c. methyl alcohol. The following results were obtained:

- (1) 0.3012 gm. cinnamic acid was weighed into a 120 c.c.



glass-stoppered bottle and 25 c.c. of the above iodine solution added. A blank containing 25 c.c. of iodine solution was measured at the same time. After standing three hours at room temperature they were titrated with N/10 thiosulphate solution.

Blank 49.76 c.c.

Cinnamic acid 47.68 c.c.

Iodine absorbed = 8.73% of weight of cinnamic acid.

% of complete theoretical addition = 5.09%.

(2) 0.2905 gm. cinnamic acid was weighed in a glass-stoppered bottle and 25 c.c. of the above iodine solution added. A blank was run as before and both were allowed to stand 8 hours at room temperature.

Titration with N/10 thiosulphate solution.

Blank 49.64 c.c.

Cinnamic acid 47.04 c.c.

Iodine absorbed = 11.32% of weight of cinnamic acid.

% of complete theoretical addition = 6.75%.

The complete theoretical addition with cinnamic acid is 171.5% of its weight. From the above tests it can be seen that the cinnamic acid does not readily absorb iodine and is not a suitable substance to use. These results agree with the Hübl number for cinnamic acid published by Benedikt and Lewkowitsch.<sup>10</sup>

b. Experiments to Confirm the Results of Gill and Adams.

With oleic acid the following tests were run:-

(3) 0.4827 gm. oleic acid purified by myself and 0.4087 gm. of Merck's best oleic acid were weighed in 120 c.c. glass-stoppered bottles and 25 c.c. of the above iodine solution added to each.





Blank was run. Time 5 hours. Temperature  $27.7^{\circ}$  C.

Titration with N/10 thiosulphate solution.

Blank 49.40 c.c.

Merck sample 24.12 c.c.

Purified sample 20.14 c.c.

Iodine absorbed by Merck sample = 76.66% of weight oleic acid

Iodine absorbed by purified sample = 78.27% " " "

% of theoretical absorption(Merck sample) = 85.11%

% of theoretical absorption (purified sample) = 86.90%.

(4) 0.4774 gm. of purified oleic acid and 0.4445 gm. of Merck's best oleic acid were weighed into 120 c.c. glass-stoppered bottles and 25 c.c. of above iodine solution added. A blank was run. Time 6 hours. Room temperature.

Titration with N/10 thiosulphate solution.

Blank 49.37 c.c.

Merck sample 19.08 c.c.

Purified sample 21.37 c.c.

Iodine absorbed(Merck sample) = 80.24% of weight of oleic acid

Iodine absorbed(purified sample) = 79.66% of weight oleic acid

% of theoretical addition(Merck sample) = 89.08%

% of theoretical addition(purified sample) = 88.44%.

These results do not agree with those obtained by Gill and Adams for they obtained almost the theoretical addition, 90.07% of the weight of the oleic acid, under the same conditions.

In order to find if it were possible to obtain the theoretical addition a series of tests were run at a higher temperature and for a longer time.



(5) 0.4429 gm. of purified oleic acid and 0.3859 gm. of Merck's pure oleic acid were weighed into 120 c.c. glass-stoppered bottles. 25 c.c. of above iodine solution were added. A blank was run. Time 3 hours. Temperature 50° C.

Titration with N/10 thiosulphate solution.

|  |  |
|--|--|
| Blank                                      | 47.65 c.c.                               |
| Merck sample                               | 18.00 c.c.                               |
| Purified sample                            | 21.15 c.c.                               |
| Iodine absorbed(Merck sample)              | $\frac{8}{86.55\%}$ of weight oleic acid |
| Iodine absorbed(purified sample)           | =86.85% of weight oleic acid             |
| % of theoretical addition(Merck sample)    | = 96.09%                                 |
| % of theoretical addition(purified sample) | = 96.43%.                                |

(6) 0.4352 gm. of purified oleic acid and 0.4339 gm. of Merck's oleic acid were weighed into 120 cc. glass-stoppered bottles and 25 cc. of above iodine solution was added. A blank was run. Time 7 hours. Temperature 50° C.

Titration with N/10 thiosulphate solution.

|   |                               |
|---|-------------------------------|
| Blank                                   | 47.95 cc.                     |
| Merck sample                            | 17.99 cc.                     |
| Purified sample                         | 17.88 cc.                     |
| Iodine absorbed(Merck sample)           | = 87.35% of weight oleic acid |
| Iodine absorbed(purified sample)        | = 87.38% of weight oleic acid |
| % theoretical addition(Merck sample)    | = 96.78%                      |
| % theoretical addition(purified sample) | = 97.01%.                     |

These results approached very near the theoretical value (90.07%).



c. Experiments to Find the Effects of Various Iodides on this Reaction.

Together with the above tests a series of tests were run to see if any other of the metallic iodides would have an effect similar to mercuric iodide. The iodides tried were those of barium, magnesium, nickel and iron. In all these cases there was practically no absorption of iodine. Either these salts prevented substitution by exerting a negative catalytic influence or they precipitated the oleic acid as insoluble oleates. A test was made with barium iodide and it was found that it would not precipitate the oleic acid in methyl alcohol solution. This fact seems to substantiate the first view.

d. Experiments to Find the Amount of Substitution in the Oleic Acid and Allyl Alcohol.

It was necessary next to determine whether the reaction was a suitable one for determining the reaction velocity. There exists a possibility that the iodine might substitute as well as add. In case of substitution every hydrogen atom liberated would unite with another iodine atom to form hydriodic acid. So to determine if there was any substitution and the amount it is only necessary to determine the amount of hydriodic acid in solution. As it is the only possible mineral acid in solution it is easily determined by adding potassium iodate and titrating the liberated iodine.<sup>11</sup>







The actual tests were carried out as follows:- after the free iodine was titrated in the manner used in the preceding tests, 5 cc. of a 10% solution of potassium iodate was added and the liberated iodine titrated with the same thiosulphate<sub>A</sub> solution. The thiosulphate<sub>A</sub> used after addition of the iodate shows the amount of iodine present as hydriodic acid. The following tests were run.

(7) 0.2169 gm. of purified oleic acid was weighed into a 120 cc. glass-stoppered bottle and 20 cc. of the above iodine solution added. A blank was also run. Time 3 hours. Room temperature.

Titration with N/10 thiosulphate solution.

Blank            38.98 cc.+ 5 cc. 10% sol.  $\text{KIO}_3$  - no iodine freed  
Oleic acid 24.92 cc.+ 5 cc. 10% sol.  $\text{KIO}_3$  - 7.10 cc.  
Iodine absorbed = 81.79% of weight of oleic acid  
Iodine substituted = 41.30% of weight of oleic acid  
Iodine added - none.

It can be seen from this test that if the free acid is due to substitution according to the opinion of Schweitzer and Lungwitz, this reaction is one of substitution entirely. No addition takes place. Another test was run using a solution of 5 gms. of iodine in 200 cc. of methyl alcohol and no catalyser.

(8) 0.2169 gm. of purified oleic acid was weighed into a 120 cc. glass-stoppered bottle and 20 cc. of the above iodine solution added. A blank was run. Time 3 hours. Temperature 30° C.

Titration with N/10 thiosulphate solution.

Blank            38.98 cc.+ 5 cc. 10% sol.  $\text{KIO}_3$  - no iodine freed  
Oleic acid 27.22 cc.+ 5 cc. 10% sol.  $\text{KIO}_3$  - 6.94 cc.



Total iodine absorption = 68.57% of weight of oleic acid.

Substitution = 34.10% of weight of oleic acid

Addition - none.

From this test it would appear that the only part the mercuric iodide played was to slightly hasten substitution. These tests were repeated using allyl alcohol,  $\text{H}_2\text{C} = \text{CH} - \text{CHOH}$ , in place of the oleic acid and similar results were obtained. A standard solution of allyl alcohol was made up in methyl alcohol so that 5 cc. of the solution contained 0.08714 gm. of allyl alcohol.

(9) To 5 cc. of above allyl alcohol solution was added 25 cc. of the above iodine-mercuric iodide-methyl alcohol solution. Time 3 hours. Temperature  $30^\circ \text{C}$ . A blank was run.

Titration with N/10 thiosulphate solution.

Blank 48.11 cc. +  $\text{KIO}_3$  sol. - no iodine freed

Allyl alcohol 26.50 cc. + 5 cc. 10% sol.  $\text{KIO}_3$  - 11.01 cc.

Total iodine absorbed 313.5% of weight of allyl alcohol.

Total iodine substituted 154.4% of weight of allyl alcohol

Total iodine added 4.7% of weight of allyl alcohol.

(10) To 5 cc. of allyl alcohol solution was added 25 cc. of the iodine-methyl alcohol solution without catalyser. Time 3 hours. Temperature  $30^\circ \text{C}$ . A blank was run.

Titration with N/10 thiosulphate solution.

Blank 36.47 cc. + 5 cc. 10% sol.  $\text{KIO}_3$  - no iodine freed

Allyl alcohol 26.25 cc. + 5 cc. 10% sol.  $\text{KIO}_3$  - 5.18 cc.

Total iodine absorbed 148.3% of weight of allyl alcohol

Total iodine substituted 79.5% of weight of allyl alcohol





Total iodine added - none.

The allyl alcohol acts much like the oleic acid. The theoretical addition number of allyl alcohol is 437.4% of the weight of the allyl alcohol. The ordinary Hübl test with the oleic acid and the allyl alcohol used gave the following results:-

Oleic acid

|                    |                                 |
|--------------------|---------------------------------|
| Iodine number      | 82.42% of weight of oleic acid  |
| Amount substituted | 11.79% of weight of oleic acid  |
| Amount added       | 58.84%.of weight of oleic acid. |

Allyl alcohol

|                    |                                    |
|--------------------|------------------------------------|
| Iodine number      | 418.4% of weight of allyl alcohol  |
| Amount substituted | 132.4% of weight of allyl alcohol  |
| Mount added        | 153.6% of weight of allyl alcohol. |

It is evident from these results that the reaction of iodine with these unsaturated compounds in methyl alcohol solution is not suitable for the purpose of determining the reaction velocity.

e. Experiments with Carbon Bisulphide as a Solvent for the Oleic Acid and Allyl Alcohol.

It was necessary to find a medium in which addition alone would take place. Following the suggestion of Sweitzer and Lungwitz<sup>12</sup> carbon bisulphide was used as a solvent. Carbon bisulphide is a good solvent for iodine and also dissolves 0.352 gm. mercuric chloride, 1.8 gms. mercuric bromide, and 3 gms. mercuric iodide per 100 cc.



The following tests were carried out:-

(11) 0.1710 gm. cinnamic acid was weighed into a glass bottle and 25 cc. of iodine-carbon bisulphide solution (5 gms. to 200 cc) added and 0.5 gm. mercuric chloride. A blank was run. Time 3 hours. Temperature 30° C.

Titration with N/10 thiosulphate solution.

|                 |                                     |                   |
|-----------------|-------------------------------------|-------------------|
| Blank           | 55.07 cc. + $\text{KIO}_3$ solution | - no iodine freed |
| Cinnamic acid   | 54.65 cc. + $\text{KIO}_3$ solution | - no iodine freed |
| Iodine absorbed | - trace.                            |                   |

(12) To 5 cc. of a solution of 0.8506 gm. of allyl alcohol in 50 cc. of  $\text{CS}_2$  was added 25 cc. of iodine in  $\text{CS}_2$  solution and 0.1 gm. of mercuric chloride. A blank was run. Time 3 hours. Temperature 30° C.

Titration with N/10 thiosulphate solution.

|               |                                     |                   |
|---------------|-------------------------------------|-------------------|
| Blank         | 55.07 cc. + $\text{KIO}_3$ solution | - no iodine freed |
| Allyl alcohol | 39.46 cc. + $\text{KIO}_3$ solution | - no iodine freed |
| Iodine added  | = 247.0% of allyl alcohol.          |                   |

(13) To 5 cc. of a solution of 0.8506 gm. of allyl alcohol in 50 cc.  $\text{CS}_2$  was added 25 cc. of iodine solution in  $\text{CS}_2$  and 0.5 gm. of mercuric chloride. A blank was run. Time 3 hours. Temperature 30° C.

Titration with N/10 thiosulphate solution.

|               |                                     |                    |
|---------------|-------------------------------------|--------------------|
| Blank         | 55.07 cc. + $\text{KIO}_3$ solution | - no iodine freed  |
| Allyl alcohol | 27.50 cc. + $\text{KIO}_3$ solution | - no iodine freed. |
| Iodine added  | = 410% of weight of allyl alcohol.  |                    |



(14) To 5 cc. of a solution of 0.8506 gm. of allyl alcohol in 50 cc. of  $\text{CS}_2$  was added 25 cc. of iodine solution in  $\text{CS}_2$  and 0.5 gm. of mercuric chloride. A blank was run. Time 3 hours. Temperature  $30^\circ \text{C}$ .

Titration with N/10 thiosulphate solution.

|   |                                     |                   |
|---|-------------------------------------|-------------------|
| Blank   | 55.64 cc. + $\text{KIO}_3$ solution | - no iodine freed |
| Allyl alcohol                                     | 27.56 cc. + $\text{KIO}_3$ solution | - no iodine freed |
| Iodine added = 403.4% of weight of allyl alcohol. |                                     |                   |

These results agreed with those of Sweitzer and Lungwitz in that no free acid was formed in the carbon bisulphide solution but it was found to be impossible to get correct results on titrating due to the fact that the addition product formed decomposed very rapidly, liberating iodine, when water and potassium iodide solution were added. The decomposition was so rapid that it made correct titration impossible. No free acid was liberated, however, when the water was added. This fact was proved by adding water and allowing to stand for sometime and then applying the  $\text{KIO}_3$  test.

Tests were run with oleic acid to see if it would give similar results:-

(15) 0.4369 gm. of oleic acid was weighed into a 120 cc. glass-stoppered bottle and 25 cc. of iodine solution in  $\text{CS}_2$  was added. No catalyser was added. A blank was run. Time 3 hours. Temperature  $30^\circ \text{C}$ .

Titration with N/10 thiosulphate solution.

|            |   |             |
|------------|---|-------------|
| Blank      | 53.30 cc. + 5 cc. 10% sol. $\text{KIO}_3$ | - no change |
| Oleic acid | 47.70 cc. + 5 cc. 10% sol. $\text{KIO}_3$ | - 0.25 cc.  |





Total iodine absorbed 16.21% of weight of oleic acid

Total iodine substituted .72% of weight of oleic acid

Total iodine added 14.77% of weight of oleic acid

(16) 0.4556 gm. of oleic acid was weighed into a 120 cc. glass-stoppered bottle and 25 cc. of iodine solution in  $\text{CS}_2$  and 0.5 gm. of mercuric chloride was added. A blank was run. Time 3 hours. Temperature  $30^\circ \text{C}$ .

Titration with N/10 thiosulphate solution.

Blank 55.30 cc. + 5 cc. of 10% sol.  $\text{KIO}_3$  - no change

Oleic acid 28.15 cc. + 5 cc. of 10% sol.  $\text{KIO}_3$  - 2.15 cc.

Total iodine absorbed 75.36% of weight of oleic acid

Total iodine substituted 5.97% of weight of oleic acid

Total iodine added 63.39% of weight of oleic acid.

The oleic acid addition product did not decompose as rapidly as the allyl alcohol addition product. There was still a slight formation of free acid.

### III. CONCLUSIONS.

From the experimental work done in this investigation the following conclusions may be drawn:-

1. The method of Gill and Adams<sup>6</sup> has no practical application as a method for the determination of the unsaturated acid present in fats and oils. The iodine absorption obtained by these



investigators has been shown to be due to substitution of iodine in the oleic acid chain-- no addition taking place under the conditions of the experiment.

2. The free acid formed in the reaction is probably due to substitution. Ingle sought to explain the formation of free acid in the Hübl and Wijs methods in the following manner:- He assumed that the addition product was first formed, then this reaction with water according to the equation below.<sup>13</sup>



This view might be applied to the iodine addition products as well as the chlorine-iodine addition products. The facts which oppose this theory are:

(a) Free acid is formed in absolute alcohol, dry ether, chloroform, and benzene solutions.<sup>12</sup> That the free acid is not formed as a product of the reaction between the water added at the time of titration and the iodine addition product is shown by the following experimental evidence.

(b) In carbon bisulphide solution no free acid was formed with allyl alcohol. When water and potassium iodide solution were added no free acid formed on standing but iodine was liberated.

The facts which favor substitution as an explanation of the free acid formed are:

(c) The amount of free acid never exceeded half of the total iodine absorption. In several cases it was exactly one half.





It seems logical, therefore, to conclude from the above evidence that the free acid formed is a result of substitution of the halogen in the chain of the unsaturated compound.

3. Certain salts seem to prevent substitution by exerting a negative catalytic influence.<sup>12</sup>



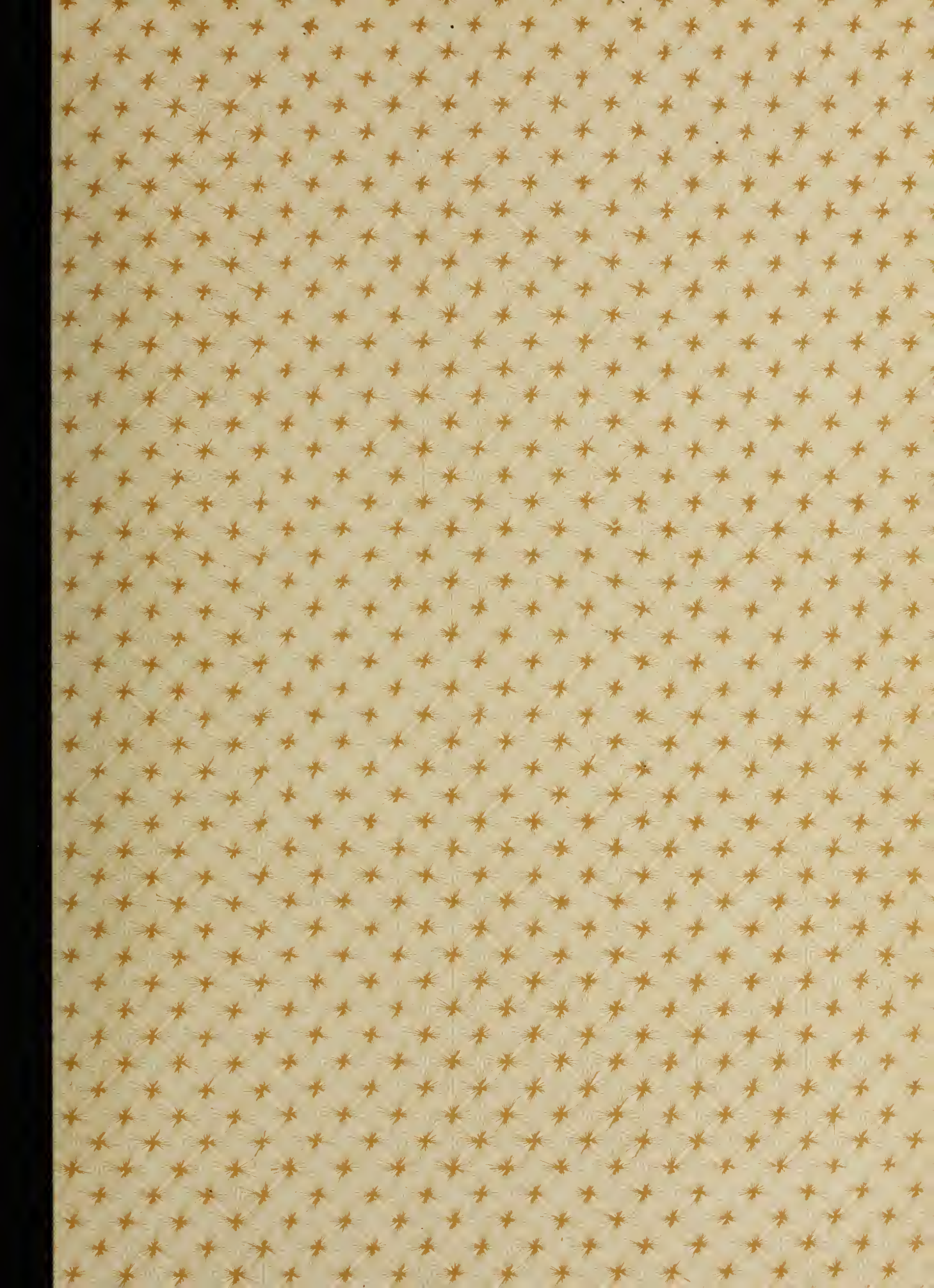
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